

# STEAM GASIFICATION OF COAL — THE EFFECTS OF ACID- AND ALKALI-LEACHING OF COAL ON ITS GASIFICATION RATE —

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## INTRODUCTION

The conversion reaction of coal to synthesis gas ( $\text{CO} + \text{H}_2$ ) is one of the most significant coal utilization processes because a wide range of coals could be applied in this process and the resulting gases are available as valuable feedstocks of chemical industry. One of the drawbacks of coal gasification is the presence of inorganic materials in coal, which cause fouling or slugging phenomena by producing scale during the gasification. Consequently, "deashing of coal" is a technically very important pretreatment for gasification. In this study we conducted acid- (HF or HNO<sub>3</sub>) and alkali-leaching of five coals, Australian Yallourn (YL), Indonesian South Banko (SB), US Illinois NO. 6 (IL), Japanese Akabira (AK), and Australian Newstan coals (NS), the treated coals of which were submitted to steam gasification.

## EXPERIMENTAL SECTION

### Coal Samples

Illinois No. 6 coal was purchased from Argonne national laboratory. Newstan original and alkali-leached coals were presented by CSIRO. Other coals were our samples and stored in a glass vessel, respectively, under nitrogen atmosphere. Reagents and solvents were commercially available and used without further purification.

### Leaching of coal with HNO<sub>3</sub>

Pulverized coal (100 mesh under, 1.5 g) and 1N HNO<sub>3</sub> (300 mL) were stirred magnetically in a 1 L flask at 130 °C for 3 h. The products were poured into a 2 L beaker containing 100 g of ice. The resulting mixture was filtered, the filter cake being washed with water until the filtrate became neutral.

### Leaching of coal with HF

A platinum crucible containing pulverized coal (100 mesh under, 2.5 g) and 46% HF (5 mL) was heated on an oil bath (90 °C) for 7 h. After the end of reaction, the resulting mixture was filtered and washed with deionized water.

### Gasification reaction

Coal (ca. 10 mg, daf base) was put on a platinum cell in the heating zone of TG apparatus (Shimadzu TF-50H), being heated from room temperature to 900 °C at a heating rate of 50 K/min. Then, steam was introduced to the system at 900 °C, being kept for about 2 h. The resulting gases were analyzed by a Shimadzu GC-8A gas chromatograph (Polarpack Q column, 6mm diameter x 3m long) connected to the TG apparatus. Using the same apparatus, pyrolytic experiments were conducted for the original and treated coals (heating from room temperature to 900 °C, 5 K/min).

### Heat treatment of the sample coals

The sample coals (1 g) were heated up to 900 °C with a heating rate of 30 K/min under a nitrogen stream (100 mL/min) by using an Isuzu DKRO-14K type tubular electric furnace. The resulting semicokes were submitted to specific surface area-measurement. Their specific surface area was measured by using argon adsorption method on a Shimadzu 2205 type analyzer.

## RESULTS AND DISCUSSION

### Deashing of the sample coals

In order to remove inorganic materials (IOM) in coal, five coals were treated by HF or HNO<sub>3</sub>, the results being shown in Figure 1. Treatment of coal with HF resulted in removal of IOM in 36-96%, while HNO<sub>3</sub> treatment resulted in 33-46% removal. It should be noted that HNO<sub>3</sub> treatment could remove sulfur in these coals, especially, in the case of IL coal known as a high-sulfur coal, where 67% of sulfur could be removed. Huffman *et al.* had reported that sulfur in IL coal composed of 37% of inorganic form (mainly pyrite) and 63% of organic form (thiophenic and sulfidic).<sup>1)</sup> The result indicates that HNO<sub>3</sub>-treatment could remove organic sulfur in the coal.

As to nitrogen and oxygen, N/C and O/C atomic ratios were increased by treatment with HNO<sub>3</sub>. FT/IR spectra of the original and treated coals revealed that nitration of aromatic rings and oxidation of alkyl side chains to carboxylic groups occurred to some extent during the treatment.

### Steam gasification of the original and treated coals

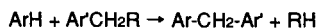
The original and treated coals were submitted to steam gasification. The reaction was conducted at 900 °C under steam flow (75.7 mmHg). Figure 1 shows a time profile for conversion of char. The order of gasification rate obeyed the following sequence: YL > SB > IL > NS > AK, this indicating that lower rank coals have higher reactivity than higher rank ones. These results agree well with the results reported by Hashimoto *et al.*<sup>2)</sup> and Tamai *et al.*<sup>3)</sup> In the case of the lower rank coals (YL and SB), HF-treatment lead to decrease their reactivity, on the other hand, HF-treatment of the higher rank coals (IL, AK, and NS) resulted in the increase of their reactivity (Figure 2). YL and SB coals contain CaO and Fe<sub>2</sub>O<sub>3</sub>, these are known to act as gasification catalysts. This might suggest that HF-leaching remove these catalyst species. As to HNO<sub>3</sub>-leaching of coal, this pretreatment could improve their reactivity to a small extent (in the case of IL, AK, and NS coals). The NaOH soaked NS coal (provided by CSIRO) was found to have higher reactivity than that of the HF- or HNO<sub>3</sub>-leached coals.

### Catalytic gasification of the original and treated coals

Catalytic gasification of the sample coals was conducted. Potassium carbonate (3 wt%) was impregnated from its aqueous solution. The results of catalytic gasification are shown in Figure 3. The catalyst increased the rate of gasification as 2-4 times. In the all coals employed, HF treated coals showed higher reactivity than those of the original coals. These are different from the results of non-catalytic reaction of the lower rank coals (YL and SB).

### Pyrolytic behavior of the sample coals

In order to examine the pyrolytic behavior of the sample coals, their TG/GC analyses (sample ca. 10 mg) were conducted (heating from room temperature to 900 °C at 5 K/min). TG curves are shown in Figure 4, the order of the rate of devolatilization obeying the following sequence; NS < IL < AK < SB < YL. Figure 4 also shows the time profiles for gas evolution (CO<sub>2</sub> and CH<sub>4</sub>). The peak of the evolution of CO<sub>2</sub> was observed at 400 °C for SB and YL coals and at 700 °C for all coals, the former peak corresponding decarboxylation. On the other hand, the peak of CH<sub>4</sub> evolution was observed at around 600 °C. The order of its rate obeyed the following sequence; YL < SB < IL < NS < AK, this corresponding the reversed sequence for the gasification rate. Solomon *et al.* had stated that lighter hydrocarbon gas evolution during pyrolysis results in formation of crosslinking.<sup>4)</sup> The reaction described in the following equation might occur and this might cause deactivation of char.



Specific surface area (SA) of pyrolytic residues from the sample coals was measured. SA was increased according to the sequence; IL (160 m<sup>2</sup>/g) < AK (235) < NS (275) < SB (713) < YL (870). This order does not agree with rank (carbon contents) or gasification rate of the sample coals. The lower rank coals have relatively larger SA value, this being resulted from decarboxylation reaction at around 400-500 °C.

Now, we are conducting TG/GC analyses of the acid- or alkali-leached coals and investigating a relationship between their pyrolytic behavior and reactivity.

### **SUMMARY**

In this study, we examined the effects of acid- or alkali-leaching of five coals (from brown to bituminous coal range) on the rate of catalytic and non-catalytic steam gasification. The results obtained were summarized below.

- 1) HF- and NaOH-leaching of coal could remove 60-90 % of inorganic materials in it. In the case of HNO<sub>3</sub>-leaching, degree of deashing was somewhat small, but this treatment could remove both inorganic and a part of organic sulfur.
- 2) Acid- and Alkali-leaching of coal could enhance the rate of non-catalytic and catalytic steam gasification to some extent.
- 3) TG/GC analyses of the sample coals showed the presence of some relationships between reactivity of char and amount of CH<sub>4</sub>-evolution during pyrolysis (related to formation of cross-linking).

### **REFERENCES**

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Table 1. Elemental analyses and ash contents of the original and treated coals

The original and treated coals					
Samples	Atomic ratio			Ash (Wt%)	Degree of deashing (%)
	O/C	N/C	S/C		
NS coal					
Original	0.079	0.022	0.003	9.2	-
HNO <sub>3</sub> -leached	0.295	0.064	0.002	6.3	33.4
NaOH-leached	0.087	0.022	0.004	0.6	93.9
HF-leached	0.102	0.021	0.003	0.4	96.4
AK coal					
Original	0.090	0.023	0.008	8.0	-
HNO <sub>3</sub> -leached	0.280	0.060	0.006	4.5	46.1
HF-leached	0.101	0.023	0.008	2.7	68.8
IL coal					
Original	0.103	0.016	0.030	16.0	-
HNO <sub>3</sub> -leached	0.364	0.065	0.010	8.6	50.8
HF-leached	0.150	0.016	0.025	4.7	74.3
SB coal					
Original	0.269	0.017	0.002	2.4	-
HF-leached	0.275	0.015	0.002	1.1	54.4
YL coal					
Original	0.310	0.006	0.001	1.6	-
HF-leached	0.360	0.009	0.001	1.0	36.4

Table 2. Composition of inorganic materials in the sample coals

Coals	Na <sub>2</sub> O	MgO	Al <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>	CaO	Fe <sub>2</sub> O <sub>3</sub>
NS coal	0.7	0.8	25.7	62.4	1.9	5.1
AK coal	1.6	2.0	26.1	55.2	2.2	6.7
IL coal	0.9	0.7	19.4	35.4	10.0	27.3
SB coal	1.3	2.1	20.0	12.8	16.6	11.5
YL coal	6.0	19.5	1.4	12.6	14.4	33.6

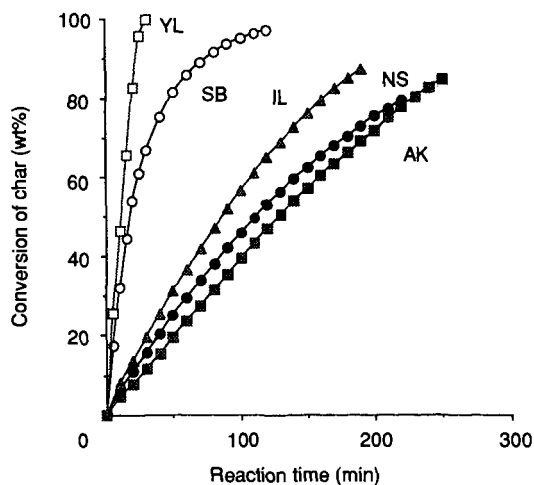


Figure 1. Time profile of steam gasification of sample coals

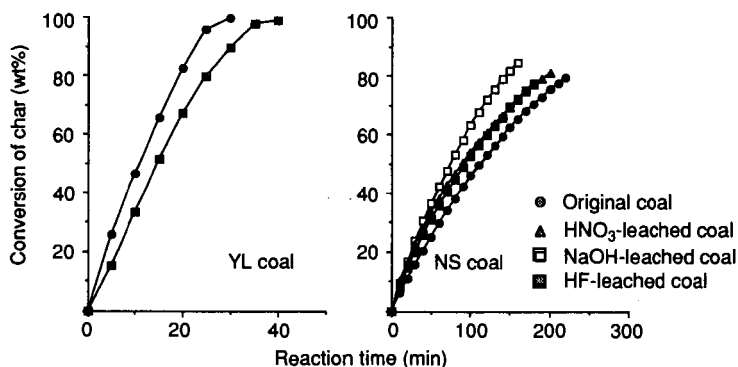


Figure 2. Steam gasification of the original and treated coals  
Catalyst  $\text{K}_2\text{CO}_3$  3wt%, 1173 K, steam flow

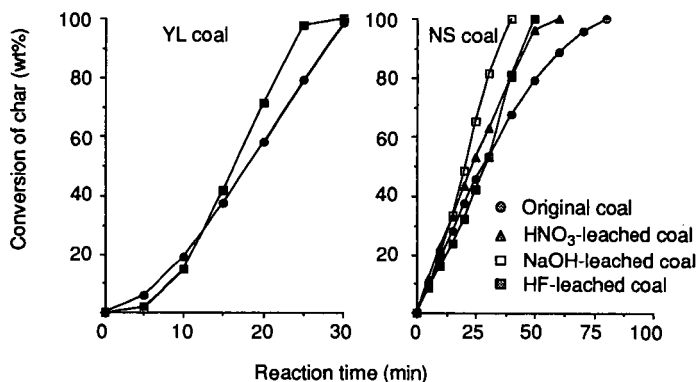


Figure 3. Catalytic gasification of the original and treated coals  
Catalyst  $\text{K}_2\text{CO}_3$  3wt%, 1173 K, steam flow

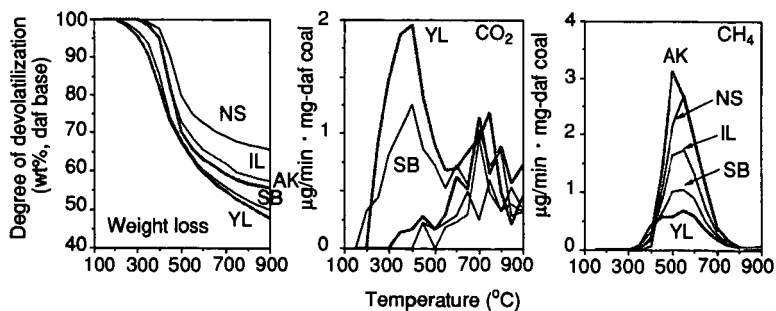


Figure 4. TG/GC analyses of the sample coals